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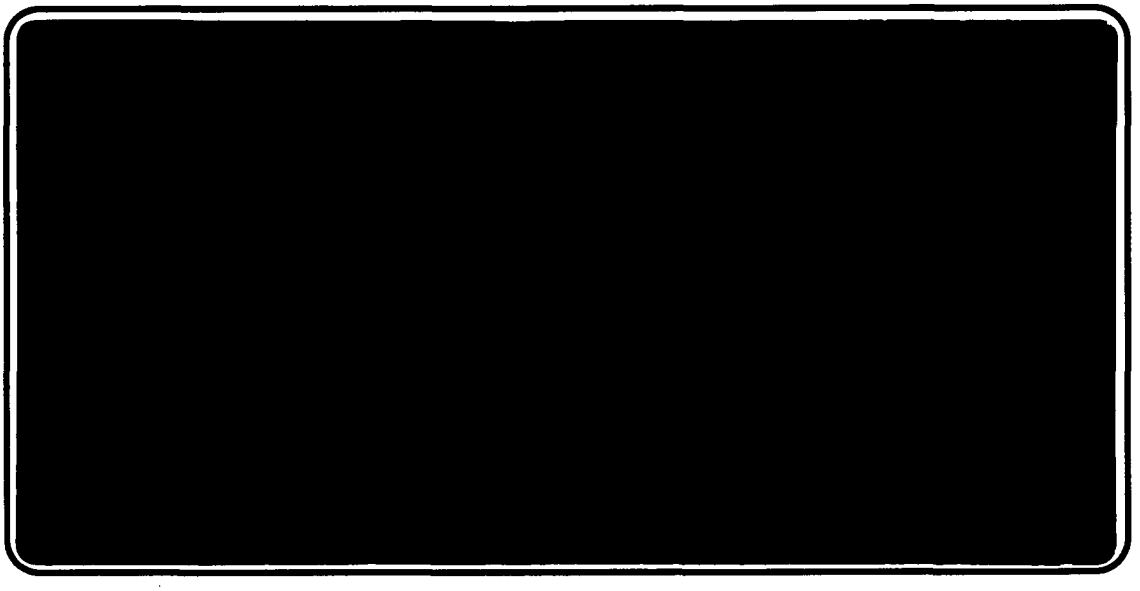

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THE SURFACE CHEMISTRY OF FLOTATION OF STICKIES AND LASER PRINTED INKS

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ABSTRACT

Removal of stickies and laser printed inks from recycled paper is facilitated by froth flotation. The efficiency of the process is shown to be a function of the surface tension of the deinking liquor and the surface energy of the contaminant. The latter is found to increase upon contact with the deinking liquor on a time scale of seconds to minutes. Possible reasons for this behavior are discussed.

INTRODUCTION

Froth flotation has been used by papermakers to remove contaminants which are too large to be washed from the fibers. To ensure high efficiency in this process, we need to understand the interrelationships among the fibers, the stickies (or inks), the deinking liquor, and the flotation cell parameters. In the present work we focus on the interactions between the contaminant and the deinking liquor.

In a theory, the details of which will be presented elsewhere, we argue that a key factor in effective flotation is strong attachment of the contaminant to the air bubble. The force of this attachment F_a is given by

$$F_a = \pi D \gamma_{LV}(1-\cos^2\theta) \qquad (1)$$

where D is the air bubble diameter, γ_{LV} is the surface tension of the deinking liquor, and θ is the contact angle between the deinking liquor and the contaminant measured through the liquid phase. The contact angle can be measured or can be calculated from the Good-Girifalco-Fowkes-Young (G-G-F-Y) equation [1]

$$\cos\theta = -1 + 2(\gamma_S^d \gamma_L^d)^{1/2}/\gamma_{LV} \qquad (2)$$

where γ_S^d and γ_L^d are the dispersion components of the solid and liquid phases, respectively.

We will test the application of equation (1) to the flotation of a series of hot melts and recycled fiber containing laser-printed ink.

MATERIALS AND METHODS

The composition of the three hot melts was determined from their FTIR spectra with the following results:

HMD - polyvinyl acetate + polystyrene + paraffinic hydrocarbon (wax or polyethylene)

HMB - glycerol ester of polymerized rosin

HME - polyethylene base

The surface energy of these stickies was determined by measuring the contact angle of a drop of methylene iodide placed on the solid and applying the G-G-F-Y equation. The values of γ_S^d for HMD, HMB, and HME were 27.1, 50.7, and 41.7 mN/m, respectively.

The deinking liquors contained 0.1% by weight sodium silicate and sufficient nonionic surfactant (Triton X-100) to achieve nominal surface tensions of 30 or 40 mN/m. The pH was adjusted to 10 or 12 with sodium hydroxide.

Contact angles of drops of these liquors on the hot melts were measured as a function of time from 5 seconds to 20 minutes. The measurements were carried out in a humidified chamber to prevent drop evaporation.

Flotation studies were conducted using a pneumatic cell developed at the Institute of Paper Chemistry. Stickies were ground and classified through screens to give particle sizes in the range of 57 to 420 μm. They were mixed with the deinking liquors for varying periods between 15 seconds and 60 minutes before flotation. Flotation was then initiated and continued for 1 minute using average bubble diameters of 260 or 350 μm.

Office waste was simulated by printing a standard pattern on alkaline-made paper using a laser printer. Pulping of this material was carried out using a LaMort laboratory pulping/flotation unit at a consistency of 10.5 % at various pH's between 8

and 12 and pulping times between 15 and 45 minutes. Flotation was carried out in the same unit at a consistency of 0.8%. Various levels of a nonionic surfactant and oleic acid were used as flotation aids and the pH was varied from 8 to 12. Flotation was continued for 10 minutes.

Standard Tappi handsheets were formed from the feed to and accepts from the flotation cell. Efficiency was evaluated by counting the number and area of ink particles in the sheets as a function of particle size class. The COCAP Dot-Counter 2.0 provided the counts in 50μm size class increments from 50 μm to >250 μm.

RESULTS AND DISCUSSION

Time Dependence of the Contact Angle

Both hot melts and laser printing toners show changes with time in their interactions with the deinking liquors. This can be monitored by following the change with time in the contact angle that a drop of deinking liquor makes with a contaminant. The results for the three hot melts at a pH of 10 and two surfactant concentrations are shown in Fig. 1.

The properties of the deinking liquor would not be expected to change appreciably with time. According to the G-G-F-Y equation, changes in the contact angle would then reflect changes in the surface energy of the contaminants. The direction of change in all cases is toward smaller contact angles or, equivalently, larger surface energies γ_S^d. To quantify these changes, we have used the time dependent contact angle data along with the appropriate value of γ_{LV} and an assumed constant value for γ_L^d of 22 mN/m to calculate a time dependent value for the contaminant's surface energy from the G-G-F-Y equation. (The experimental justification for this will be reported elsewhere.)

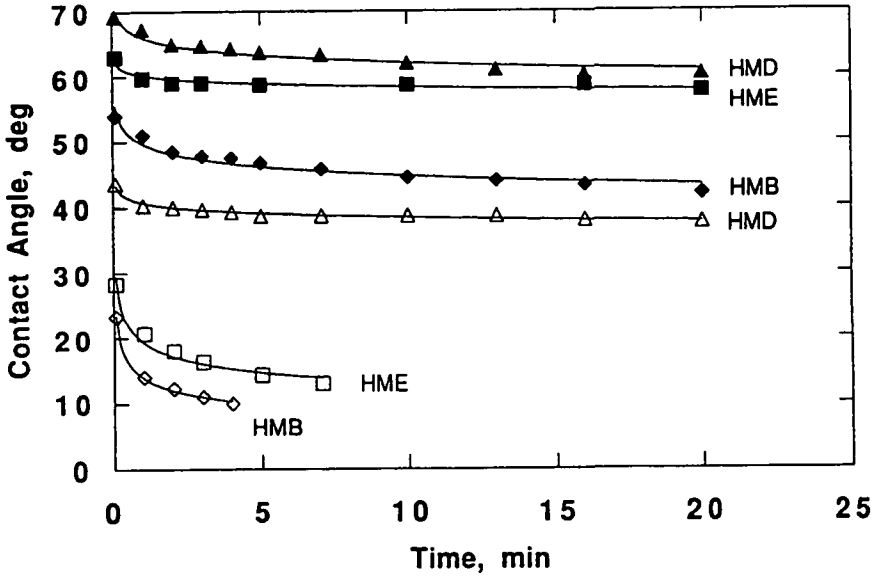

Fig.1. Time dependence of the contact angle between various hot melt adhesives and two deinking liquors. Closed symbols: γ_{LV} = 39.4 mN/m; open symbols: γ_{LV} = 29.7 mN/m.

Representative results are shown in Figs. 2 and 3 for HMB and HMD, respectively. Although the results are rather different for the two hot melts as might be expected from their compositions, there are some common trends.

a) The surface energy calculated from the contact angle at 5 seconds depends on the relative magnitudes of the surface energies of the liquor and the sticky. Stickies with (intrinsic, i.e. the value determined with methylene iodide and indicated in Fig. 2 and 3 by arrows) surface energies less than the deinking liquor attain larger values in the presence of the liquor and vice versa. The greater the difference between liquor and sticky surface energies, the greater the change in the latter's properties in the presence of the liquor. A potential explanation is that surfactant molecules adsorb on the sticky's surface in an orientation that tends to minimize the difference between the surface energies of the liquor and the sticky. For a low energy surface (HMD) the polar portion of the surfactant would be oriented toward the liquor, while the reverse would be found for high energy surfaces.

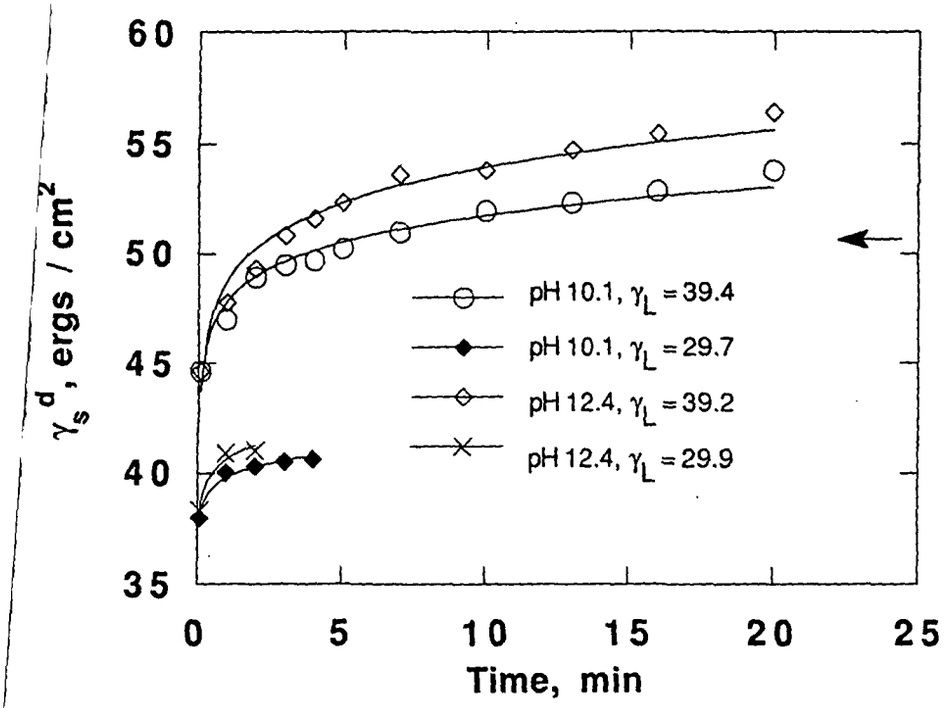

Fig.2. Calculated time dependence of HMB surface energy.

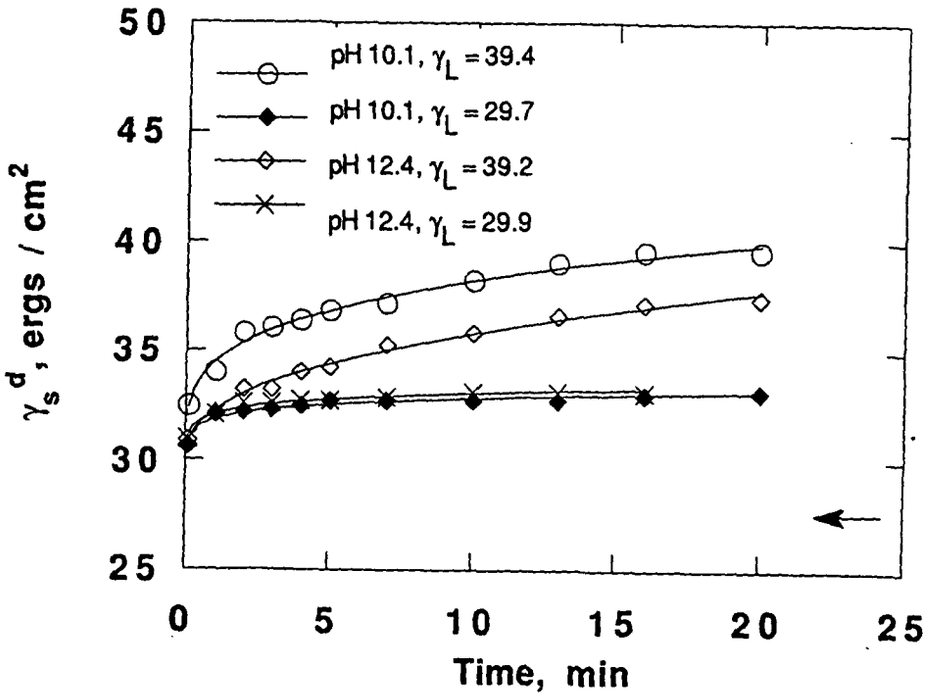

Fig. 3. Calculated time dependence of HMD surface energy.

b) In the presence of high surfactant concentration no further changes with time occur after five minutes or less. In contrast, at the low surfactant concentration changes continue to 20 minutes or beyond.

c) Effects of pH are evident at low but not at high surfactant concentration.

There are at least four possible explanations for the change of surface energy with time.

1) Surfactant may adsorb onto the surface of the sticky. The hydrophobic "tails" of the surfactant molecules would tend to adsorb on the sticky surface with the hydrophilic "head" oriented toward the solution (drop of liquor). (However, see the comments under a) above.) This process should be determined by the rate of diffusion of the surfactant molecules and, therefore, should occur on a time scale of the order of seconds or less. The experimental time scales on the order of minutes suggest this explanation is unlikely.

2) Polar species may diffuse from the bulk of the sticky to its surface. Contact with the aqueous solution would be the driving force. Hot melt adhesives are a complex mixture of materials, some more polar than others. Even a "simple" material like polyethylene contains antioxidants, residual polymerization catalyst products and perhaps other additives. The diffusion rate of these polar materials will depend upon their molecular weight and upon the segmental mobility of the major components of the sticky. This mobility in turn depends upon the glass transition temperature of these components. The potential contribution of this mechanism to the observed time dependence would be difficult to estimate without detailed compositional information.

3) Ester groups may hydrolyze. For those stickies comprised of esters (e.g. HMB) this would appear to be a likely mechanism. The pH of the deinking liquors studied ranged from 10 to 12, prime conditions for the hydrolysis of esters. The reaction would produce hydroxyl and carboxylate groups, both more polar then the ester moiety, and would lead to an increase in surface energy. The dramatic increase in surface energy of oxidized polyethylene upon ionization of the carboxyl groups has been recently shown [2]. However, hydrolysis at room temperature even at high pH is very slow and probably would not explain the observed effects. In addition, a) the lack of a pH effect at the high surfactant concentration and b) the higher surface energy at pH 10.1 for HMD which contains hydrolyzable polyvinyl acetate imply that other mechanisms may be more important.

4) Molecules in the surface may reorient. In the last decade it has been shown experimentally that molecules in the surface layer of a solid possess a finite mobility, and their orientation can be influenced by an adjacent liquid phase. This work has been reviewed [3], and an application to flexographic plates has recently been shown [4]. Molecules in the solid phase, having both polar and nonpolar groups, tend to orient their nonpolar groups toward an air interface. When this solid is placed in contact with a polar liquid, the molecules reorient to present their polar portions toward the interface. This results in an increase in the surface energy. For polymeric materials the entire chain does not reorient, but only small segments of it do. These might be composed of one to three monomer units or might be side chains. A polymer below its glas transition temperature may have sufficient local mobility at room temperature for this to occur. For example, "secondary transitions" corresponding to reorientation of side chains or portions of side chains can take place well below the glass transition temperature. Typically, the reorientation can be reversed by replacing the polar liquid by a nonpolar one or by air. Thus molecules or groups in the surface layer of an amorphous solid may have a finite mobility, and their orientation can be influenced by the adjacent phase.

It appears likely that some of the changes seen in Figs. 2 and 3 may be a result of this reorientation mechanism. Obviously, the presence of the surfactant in the solution and its orientation (polar head toward or away from the surface) when adsorbed greatly increase the complexity of the system. Without further specific information about surfactant adsorption and hot melt composition and composition homogeneity, it is not possible to offer detailed interpretation for the time dependence. It is likely that all four explanations suggested may contribute and that their relative importance depends on the specific sticky material.

Similar time dependent changes were observed for the laser printing toner in contact with the deinking liquors.

Flotation Studies

The efficiency of the flotation of the hot melts was determined by a gravimetric mass balance. The results are shown in Fig. 4 plotted against the product of factors given in eq.1. Here the contact angle used was taken from the time dependent data (Fig. 1 or equivalent) for the appropriate hot melt/deinking liquor contact time. A variety of

conditions of pH, liquor surface tension, and time of agitation prior to flotation were used on the three hot melts. The product of factors given by eq. 1 reduces the data to a single curve. Removal efficiency improves with increasing strength of attachment with most of the change occurring over a narrow range of forces. (The curve shown is a least squares fit to the hyperbolic tangent function.)

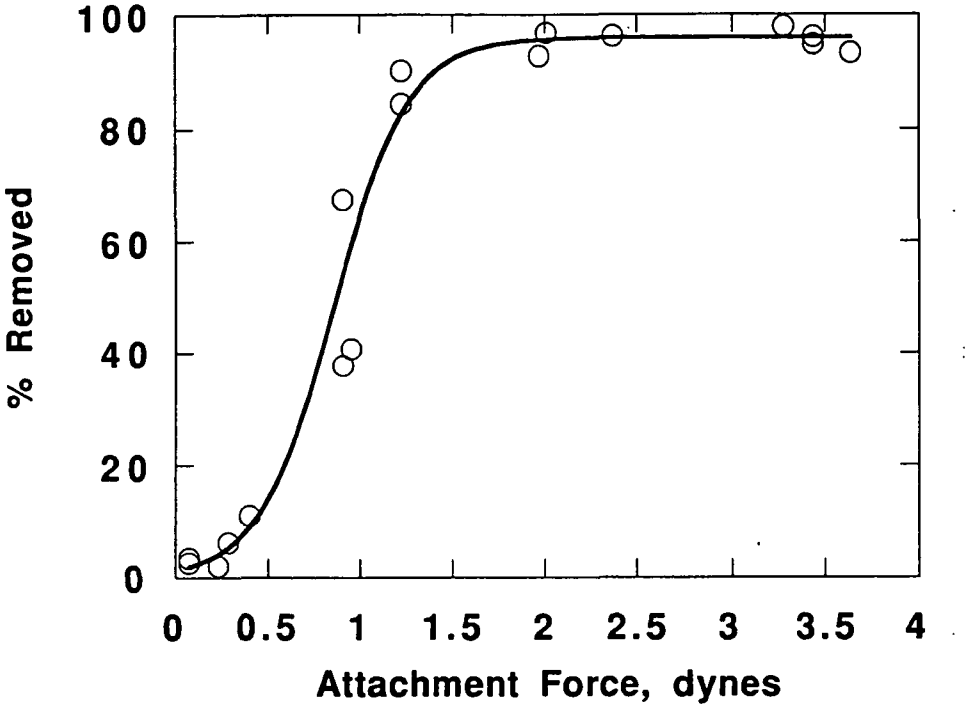

Fig. 4. Dependence of flotation efficiency of hot melts on calculated attachment force.

Although the dependence of removal efficiency on attachment force is believed to be a general relation, the particular "critical" force will be a function of the specific parameters of the flotation system. These parameters would include the ratio of bubble to particle size, mixing conditions in the flotation cell, and the duration of flotation. We are presently investigating the sensitivity of flotation to these factors.

A similar plot of removal efficiency of the laser printed ink in shown in Fig. 5 for ink particles in the size range of 50 to 100 μm. The ratio of attachment force to bubble diameter is used as the abscissa since we did not measure the average bubble size. The study covers a much narrower range of attachment forces than for the hot melts the results for which are shown for comparison. The toner shows a leveling-off in

efficiency at about 65%. This result may be indicative of more vigorous agitation conditions in the La Mort cell compared with the IPC cell or may represent non-optimum flotation chemistry.

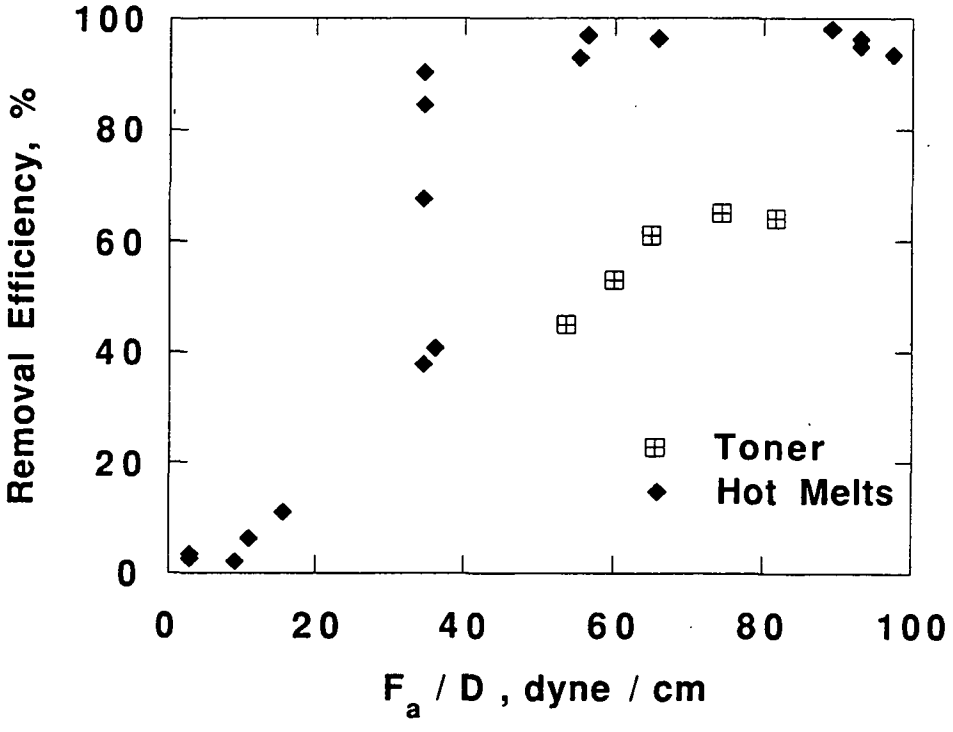

Fig. 5. Comparison of flotation efficiencies of laser printing toner and hot melts as a function of reduced attachment force.

It is of interest that there was a net increase in the number and area of toner particles of size class >250 μm in the accepts compared with the feed stream to the cell. Apparently, aggregation was occurring during the flotation process and these large particles were not efficiently removed. This may be another indication of incorrect flotation chemistry.

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